NATIONAL BUREAU OF STANDARDS REPORT

9916

Progress Report

on

X-RAY-OPAQUE REINFORCING FILLERS

FOR COMPOSITE MATERIALS

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Cryogenics[2]—Radio Physics[2]—Radio Engineering[2]—Astrophysics[2]—Time and Frequency.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:

Analytical Chemistry—Polymers—Metallurgy — Inorganic Materials — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,[3] a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:

Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation— Weights and Measures — Engineering Standards—Vehicle Systems Research.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:

Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.
[2] Located at Boulder, Colorado 80302.
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
311.05-11-3110560	June 30, 1968	9916

Progress Report

on

X-RAY-OPAQUE REINFORCING FILLERS
FOR COMPOSITE MATERIALS

By

R. L. Bowen* and G. W. Cleek**

* Research Associate, American Dental Association Research Div. at the National Bureau of Standards, Washington, D. C.

** Chemist, Inorganic Glass Section, National Bureau of Standards, Washington, D. C. 20234.

This investigation is part of the dental research program conducted by the National Bureau of Standards, in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

X-ray-Opaque Reinforcing Fillers for Composite Materials

R. L. Bowen and G. W. Cleek

Clear, colorless glasses that absorb roentgen rays were prepared by melting together compounds yielding silica, boric oxide, alumina, barium oxide and barium fluoride. Barium made the glasses radiopaque, fluoride lowered the refractive indexes, and alumina tended to stabilize the glasses. These glasses are part of the reinforcing fillers for composite dental restorative materials.

Roentgenograms have been practically useless in the detection of the secondary caries or underlying decalcified dentin that might be a sequellae to the placement of unreinforced direct filling resins or the first composite materials to become available. This is due to the fact that these materials are relatively radiolucent; consequently, there has been a continued interest in means of making such restorative materials radiopaque.

The introduction of inorganic reinforcing fillers into resin restorative materials,[1] commonly called composite materials,[2] suggested the possibility of making such materials opaque to X-rays. This can be done by the incorporation of an element of relatively high atomic number or weight into the glass that constitutes part or all of the reinforcing filler. Many of such elements are not suitable because of the color they impart to the glass, or, in the case of lead, because of the possibility of discoloration through the formation of sulfides.

The purpose of this paper is to report investigations of various barium-containing glasses, especially formulated for use in dental composite materials.

Normally, the introduction of barium oxide into a glass formulation raises its refractive index. The commercially available glasses containing the required amount of barium have refractive indexes that are above optimum for the purposes of this application. Furthermore,

most commercial barium glasses contain alkali elements, such as sodium, potassium or lithium and these elements can catalyze the hydrolysis of silica.[3] The presence of these monovalent alkali elements in a glass formulation, in the opinion of the authors, might be detrimental to the durability of the bond between the glass and the silane coupling agent. The quality of the bonding between the polymer and the filler particles determines whether or not the filler is a reinforcing filler, and is of utmost importance in determining the strength of the composite material.[4]

Since the introduction of the fluoride ion into glass formulations lowers the refractive index,[5,6] it was important to determine if clear glasses having the proper value of refractive index could be formulated utilizing barium fluoride in the place of barium oxide. Other possible effects of the fluoride ion concentration[3] remain to be determined.

MATERIALS AND METHODS

The formulations of the glasses that were prepared in this project are given in the Table. The glasses were melted in an electric furnace in a platinum crucible 6.35 cm in diameter by 7.62 cm deep. After the batch was melted, the melt was stirred with a motor-driven platinum 10%-rhodium double-bladed propeller-type stirrer to obtain homogeneity. The time of melting and fining depended on the characteristics of the melts as did the maximum temperature used. Usually, about 1.5 hours was required to fill the crucible and about the same length of time for stirring the melt. The maximum temperature used was about 1550°C but this was decreased to about 1150°C for the melts containing a relatively large amount of fluoride. A small amount of the molten glass was poured into a metal mold, and the rest was poured into clean water to quench the glass and break it up into small pieces so that it could be conveniently ground in a jar mill.

The refractive indexes were determined with a microscope by the oil-immersion method.

RESULTS

From the data given in the Table, it appears that clear glasses containing large proportions of barium fluoride can be prepared. Some of these compositions have refractive indexes close to those of the polymeric binders of current and experimental composite materials (n_D^{25} about 1.55; the refractive index of the polymeric binder varies somewhat depending on its chemical composition, extent of polymerization, water content and other factors).

Glasses containing 24 to 28 mole percent of barium fluoride or oxide, if used as the sole reinforcing filler for a dental composite material, yield materials that are more radiopaque than necessary. As a first estimate, about one part by weight of such a barium-containing glass (as a silane-treated powder) combined with two parts of silane-treated fused silica yields a composite restoration with a radiopacity intermediate between that of enamel and dentin.

The powder of one of these glasses (F1515) was passed through an oxygen-acetylene flame, converting the irregular-shaped particles into spheres. This was done because the use of rounded particle shapes and an intermittant size-distribution (gap grading) has been shown[7] to give an increase in the powder-to-liquid ratio. However, as a result of this high temperature processing, the refractive index of the glass beads formed was higher than that of the starting material. Presumably, the molten glass particles had lost some of their fluoride, possible as volatile BF_3 or SiF_4. Subsequently, a lower-temperature flame and a shorter residence time will be used to prepare spheres of the F1519-1 composition, which has been selected for further investigation.

DISCUSSION

An ideal glass for use as a reinforcing filler would have, among other desirable properties, a refractive index (to visible light) very close to that of the polymer matrix of the composite restoration. It should be colorless or have a color suitable for use in matching the color of the

composite material with that of the tooth. It should be transparent and have a low coefficient of thermal expansion. Since barium-containing glasses have higher thermal expansions that does fused silica, the total barium content of the composite should be no more than necessary to yield a composite with optimum radiopacity; one would expect this to fall in the range between that of enamel and dentin. Glass compositions that meet these particular requirements could not be found in the available literature.

A moderate alumina content has been shown to stabilize fluoride glasses against phase separation or devitrification that would be objectionable in this application.[5,6] Formulations that yield two immiscible liquids in the molten stage must be avoided.[8]

It would be desirable to make use of the "boric oxide anomaly"[9-14] and the less-well-known "alumina anomaly"[10,12-14] to obtain a glass with the lowest possible

coefficient of thermal expansion. Whether or not a matching of the molar proportions of BaO and BaF_2 with the Al_2O_3 plus B_2O_3 in the glass[13,14] gives a minimal thermal expansion has yet to be determined.

CONCLUSIONS

X-ray-opaque glasses can be prepared that are clear and colorless and that have refractive indexes suitable for use in composite restorative materials. The batch composition for one such glass, for example, is: SiO_2, 44; BaF_2, 28; B_2O_3, 16; and Al_2O_3, 12, in mole percent. The refractive index is influenced by the thermal history of the glass.

REFERENCES

1. Bowen, R. L.: Development of an Adhesive Restorative Material, in Adhesive Restorative Dental Materials II, University of Virginia Workshop, Public Health Service Publication No. 1494, 1966, pp 225-231.

2. Broutman, L. J., and Krock, R. H.: Modern Composite Materials, Reading, Mass: Addison-Wesley Pub. Co., 1967.

3. Alexander, G. B.: Polymerization of Monosilicic Acid, J Am Chem Soc 76:2094-6, 1954.

4. Bowen, R. L. Properties of a Silica-Reinforced Polymer for Dental Restorations, J Am Dent Assoc 66:57-64, 1963.

5. Cleek, G. W., and Scuderi, T. G.: Effect of Fluorides on Infrared Transmittance of Certain Silicate Glasses, J Am Ceramic Soc 42:599-603, 1959.

6. Tooley, F. V.: Handbook of Glass Manufacture. Vol. II, New York: Ogden Pub., 1960.

7. Bowen, R. L.: Effect of Particle Shape and Size Distribution in a Reinforced Polymer, J Am Dent Assoc 64:481, 1964

8. Charan, R.: Handbook of Glass Technology, 3rd Edition, Banaras (India): Banaras Hindu University Press, 1956.

9. Weyl, W. A., and Marboe, E. C.: The Constitution of Glasses, Vol. I, New York: Interscience Publishers, 1962.

10. Morey, G. W.: Properties of Glass, New York: Reinhold Publishing Corporation, 1954.

11. Hamilton, E. H.; Cleek, G. W.; and Grauer, O. H.: Some Properties of Glasses in the System Barium-Oxide Boric Oxide-Silica, J AM Ceramic Soc 41:209-215, 1958.

12. Galant, E. I.: Refractive Index and Coordination Transformation in Aluminoborosilicate Glasses, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 451-453.

13. Appen, A. A., and Fu-si, Kan: Borate and Aluminoborate Anomalies of the Properties of Silicate Glasses, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 445-450.

14. Demkina, L. I.: Additivity of the Properties of Silicate Glasses in Relation to Their Structure, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 40-45, 472.

15. Levin, E. M., and Cleek, G. W.: Shape of Liquid Immiscibility Volume in the System Barium Oxide-Boric Oxide-Silica, J Am Ceramic Soc 41:175-179, 1958.

<u>TABLE</u> Compositions and Properties of Glasses Arranged According to Decreasing Refractive Indexes

Glass No.	Composition of Batch (mole percent)						Refractive Index	Appearance
	Al_2O_3	BaF_2	BaO	B_2O_3	SiO_2	Other	n_D	
E1722*			28	24	48		1.618	clear
F 700			28		66	6 ZnO	1.605	clear
F1510		4	24	24	48		1.601	clear
F1511		6	22	24	48		1.596	semi-opaline
F1519		8	20	24	48		1.594	opaline
F1512	3	8	20	24	45		1.592	clear
F1252	10	2	25		63		1.586	clear
F1513	4	12	16	24	44		1.580	clear
F1149	10	4	20		66		1.568	clear
F1150	10	6	18		66		1.564	clear
F1515	12	20	8	16	44		1.564	clear
F1523	4		7	17	56	7 TiO_2 9 MgO	1.562	opaline and heterogeneous
F1519†	12	28		16	44		1.562	clear
F1511	10	8	16		66		1.560	clear
F1514	3	8	12	24	53		1.560	opaline
F1152	10	10	14		66		1.555	clear

Glass No.	Composition of Batch (mole percent)						Refractive Index n_D	Appearance
	Al_2O_3	BaF_2	BaO	B_2O_3	SiO_2	Other		
M3-4189†	12	28		16	44		1.554	clear
F1524	4		17	13	66		1.550	nearly clear‡
F1519-1†	12	28		16	44		1.548	clear
F1516	12	20		16	48	4MgO	1.541	trace opalescence
F1522	12		15	16	57		1.540	nearly clear‡
M14-1441†	12	28		16	44		1.539§	clear
							1.535‖	clear
F1527			17	17	58	8 AlF_3	1.536	opaline
F1526			17	13	62	8 AlF_3	1.528	opaline
F1520		28		8	43	21 AlF_3	1.518	opaline
F1521	8		7	12	73		1.500	nearly clear‡

* The data on Glass No. E1722 were taken from the literature[8]; the other data have not been published previously.

† Higher temperatures were used in the preparation of Glass No. F1519 relative to Glass No. F1519-1. Melt M14-1441 prepared in the Experimental Melting Department of Corning Glass Works was larger than their test melt M3-4189. Since these four glasses had the same batch composition, the differences in refractive index are presumably due to differences in retained fluorine with larger melts and lower temperature resulting in less volatilization of compounds such as BF_3 and SiF_4.

‡ Contained small bubbles (seeds) and small crystalline contaminations of unmelted batch material (stones) due to high melt viscosity.

§ Annealed sample.

‖ Quenched and jet pulverized.

DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS